Surfactant structure and aggregation behavior

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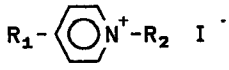
CHAPTER 7

THE RELATION BETWEEN SURFACTANT STRUCTURE AND AGGREGATE PROPERTIES FOR 1-ALKYL-4-ALKYLPYRIDINIUM IODIDES

7.1 Introduction

In the previous chapters a rather detailed study of the aggregation behavior of twenty-seven 1-alkyl-4-(or 2-)alkylpyridinium halide surfactants has been presented.



The structure of the surfactant has been varied in different ways. (i) The 4-alkyl chain has been branched while the number of carbon atoms has been kept constant, resulting in a change of the shape of the surfactant molecule. The hydrophobicity is barely affected and the headgroup has not been altered in this series of surfactants. By using this approach the hydrophobic effect, the driving force for surfactant aggregation, has been kept almost constant. (ii) The hydrophobicity of the 4-alkyl chain has been altered while both the headgroup and the overall shape of the surfactant remain invariant. (iii) The hydrophobicity of the 1-alkyl group has been increased while the hydrophobicity of the 4-alkyl chain remained invariant. (iv) The counterion has been changed. (v) The substitution pattern of the pyridinium ring has been altered. (vi) An ester group has been inserted between the pyridinium ring and the 4-alkyl chain and length of this chain has been altered. The effects caused by these systematic changes on the morphology of the aggregate have been examined and critically discussed.

The conclusions presented in the preceding chapters will be briefly outlined in this final chapter. The author's view on the structure of a spherical micelle, the relation between the shape of a surfactant and the

morphology of the aggregate, and the driving force for both micelle formation and micellar growth will be presented.

7.2 *The relation between surfactant structure and properties of spherical micelles*

The understanding of the effect of alkyl chain branching on various properties of spherical micelles contributes significantly to the knowledge about the precise structure of micelles. Particularly amazing is the finding that the free energy of micellization (as expressed in the CMC) is not significantly affected by alkyl chain branching, even though the packing of the alkyl chains is significantly altered. Only a small destabilization of the micelle upon branching is observed. This stems solely from the slightly less unfavorable hydration of branched surfactant monomers compared to that of the unbranched one, because less apolar area is exposed to water.

Furthermore, the aggregation number (n) of a spherical micelle decreases upon branching. Very good agreement with experimental values is obtained from calculations of this aggregation number, when it is assumed that a micelle can be considered as a sphere of which the radius is solely determined by **r**, the length of a fully stretched surfactant molecule. The sphere is *completely* filled with monomers. The aggregation number decreases upon branching, because the volume of the sphere becomes smaller (**r** decreases) whereas the volume of the monomer remains invariant.

These observations imply that the alkyl chains of the surfactant molecules are quite randomly oriented in the micelle with the possibility of backfolding of the chain end to the micellar surface. This rules out the micelle models of Fromherz, and Dill and Flory. Naturally, the first chain segments are anchored by the headgroups to the micelle-water interface. The degree of order of these segments is higher than that in liquid hydrocarbon. The absence of significant water penetration into the core of the micelle is in disagreement with the micelle model of Menger.

The micropolarity in the Stern region (as deduced from the position of the charge-transfer absorption band of the pyridinium iodide) is ethanol-like

and is independent on the shape of the surfactant and the hydrophobicity of the 4-alkyl and that of the 1-alkyl chain. In principle the same micropolarity should be obtained using a kinetic probe. In contrast, the catalytic efficiency of a spherical micelle towards the decarboxylation of 6-nitro-benzisoxazole-3-carboxylate is dependent on the hydrophobicity of the 1-alkyl group. Therefore, one must be very careful in using (kinetic) probes to delineate the micropolarity in the Stern region since slight differences in binding sites are amplified in the catalytic effect. Clearly the use of a surfactant containing an intrinsic probe is preferred for the determination of the micropolarity in the Stern region.

Surface potentials of spherical micelles reflect small changes in the surface charge densities upon alkyl chain branching. These potentials can be estimated from the charge density and the CMC using the "dressed micelle" model based on the non-linear Poisson-Boltzmann relation.

Thus, it is found that a spherical micelle formed from branched surfactants may be described by the same "dressed micelle" model and shows the same micropolarity of the Stern region as those formed from linear surfactants. The stability of these micelles can be easily understood from simple transfer parameters. Differences between the micelles are found in the packing of the alkyl chains and in the binding of (kinetic) probes. This indicates that micelles formed from branched surfactants are well-defined aggregates whose structure, size, and Stern region is determined by the balance between the hydrophobic effect (mainly London-dispersion interactions) and headgroup repulsion. The results of this study strongly support the micelle model of Gruen.

7.3 *The relation between surfactant structure and the morphology of an aggregate*

Branching of the alkyl chain reveals the importance of geometrical constraints in determining the *morphology* of the aggregate. It appears that the entire range of spherical micelles, rod-like micelles, and vesicles can be formed from a single class of *isomeric* surfactants, the 1-methyl-4-(C_{12}-alkyl)pyridinium iodides. The relation between the aggregate type and the shape of a surfactant may be quantified by expressing the shape of a surfactant in a molecular packing parameter (P) as suggested by Israelachvili for linear compounds. This approach also works remarkable well for branched surfactants. As a matter of fact, the relation between surfactant shape and aggregate morphology emerges in a much "purer" form from this study, since both the total number of carbon atoms and the headgroup are kept constant upon branching of the alkyl chain. A novel combination of the approach of Israelachvili with the ladder model is necessary to understand the dependence of the aggregate type on the surfactant concentration. Thus, in summary: surfactants with $P \leq 1/3$ associate into spherical micelles which do not grow upon increasing the surfactant concentration; surfactants with $1/3 < P \leq 1/2$ associate into spherical micelles which grow upon increasing surfactant concentration; and surfactants with $1/2 < P \leq 1$ aggregate into bilayers. In accord with the ladder model, the morphology of the aggregate does not depend on the alkyl chain length (n_c), although the thermodynamic stability of the aggregate is affected. The dependence of the CRC on n_c solely originates from the dependence of the aggregation number of the spherical micelle on n_c.

The possibility for backfolding determines the morphology of the aggregate in cases where the headgroup substituent (1-alkyl chain) is varied and the 4-alkyl chain is kept constant (*n*-dodecyl). Preferential bilayer formation is found when backfolding occurs, otherwise spherical micelles are formed which grow into rod-like micelles at increasing surfactant concentrations.

Interestingly, the morphology of the aggregate does not affect the micropolarity of the Stern region. The catalytic efficiency for

decarboxylation (*vide supra*) is, however, dependent on the morphology of the aggregate. Different binding sites of the probe account for this dependence.

Surfactants associate into bilayers instead of micelles when an ester group is inserted between the unbranched 4-alkyl chain and the pyridinium ring. This aggregation behavior is, as expected, independent on the length of the 4-alkyl chain (n_c = 10-16). Interdigitated packing of the alkyl chains, resulting in a change of the geometrical constraints for packing into a bilayer, is probably the origin for this remarkable aggregation behavior for an unbranched, single chain surfactant.

7.4 The driving force for surfactant association and micellar growth

Surfactants associate into aggregates of relatively well-defined size and shape as a result of a delicate balance of repulsive and attractive forces, coupled to specific regions of the surfactant molecule in the aggregate. Unexpectedly, the temperature dependence of the CMC is small. This is unexpected because it is quite in contrast to the common view that the release of structured water from the hydrophobic hydration shells of the alkyl chains is the origin of the hydrophobic effect. Although this release of structured water results indeed in the striking positive value of the entropy of micellization, the overall effect on the free energy of micellization is of minor importance due to enthalpy-entropy compensation. It seems clear from the temperature dependence of the CMC of 1-methyl-4-(C_{12}-alkyl)pyridinium iodides that London-dispersion interactions between the apolar alkyl chains are the origin of the attractive interaction which drives surfactants into aggregates.

The free energy of transfer of a methylene group from water to the aggregate may be separated from other contributions to the free energy of micellization. This free energy is independent of the morphology of the aggregate. However, this free energy does depend on the position of the CH_2 group in the aggregate (Stern region vs. core) and on whether the methylene group is located in the main chain or in the side chain of a surfactant monomer.

The ladder model may be used in a quite novel way to calculate the

enthalpy of the sphere-to-rod transition (ΔH_{sr}) from the temperature dependence of the CRC. These enthalpies are in good accord with experimental ones. ΔH_{sr} reflects a reduction of the apolar part exposed to water at the sphere-to-rod transition. The driving force for micellar growth is the reduction of this area. For surfactants having a high P value, ΔH_{sr} becomes more exothermic and more of this exposed area may be reduced compared to those having a low P value. The former surfactants pack better into a rod-like micelle, resulting in less water penetration, than the surfactants which have a low P value.

It is the author's contention that these conclusions are not only valid for the 1-alkyl-4-alkylpyridinium iodides, but may be quite general for a large variety of surfactants.